

Electronic Supplementary Material (ESI)

Supporting Information

**Fluorescent Carbon Nano Dots from Lignite: Unveiling the
Impeccable Evidence for Quantum Confinement**

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Figure S1. Characterisation of Lignite.

Figure S2. TEM image of Pristine solution obtained after reflux indicating the existence of both CNPs and layered structure of lignite, TEM image of CNP2 Solution before ethanol extraction & FTIR spectrum of Lignite and CNP1.

Figure S3. Characterisation of CNDs.

Figure S4. Statistical particle size distribution of CNP1, CNP2 & CD3.

Figure S5. Schematic representation of experimental setup for PLAL.

Figure S6. Excited Wavelength dependent emission spectrum of CNP1 & CNP2. Emission wavelength dependent excitation spectrum CNP1, CNP2 & CD3.

Figure S7. 2D Fluorescence Topographical Map of CNP1, CNP2, CD3_LC, CD3_MC, CD3_HC & CD3M.

Figure S8. Characterisation of CD3M.

Figure S9. Fluorescence lifetime decay of **a)** CNP1 **b)** CNP2, recorded by exciting at 266 nm and monitored at different wavelength.

Figure S10. Fluorescence lifetime decay of **a)** CNP1 **b)** CNP2 **c)** CD3, recorded by exciting at 375 nm and monitored at different wavelength.

Figure S11. Absorption spectrum of CD3M measured through reflectance mode.

Figure S12. Variation in the emission spectrum of CD3M with respect to time at different relative humidity.

Figure S13. Phosphorescence lifetime decay of CD3M, recorded by exciting at 360 nm and the inset showing the corresponding standard deviation.

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Table S6. Fluorescence Lifetime data of CNP1 measured at different monitoring wavelength by exciting at 266 nm.

Table S7. Fluorescence Lifetime data of CD3 measured at different monitoring wavelength by exciting at 375 nm.

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Table S10. Features of CNPs exfoliated by pulsed laser ablation on different carbon sources.
Procedure for 2D fluorescence topographical mapping.

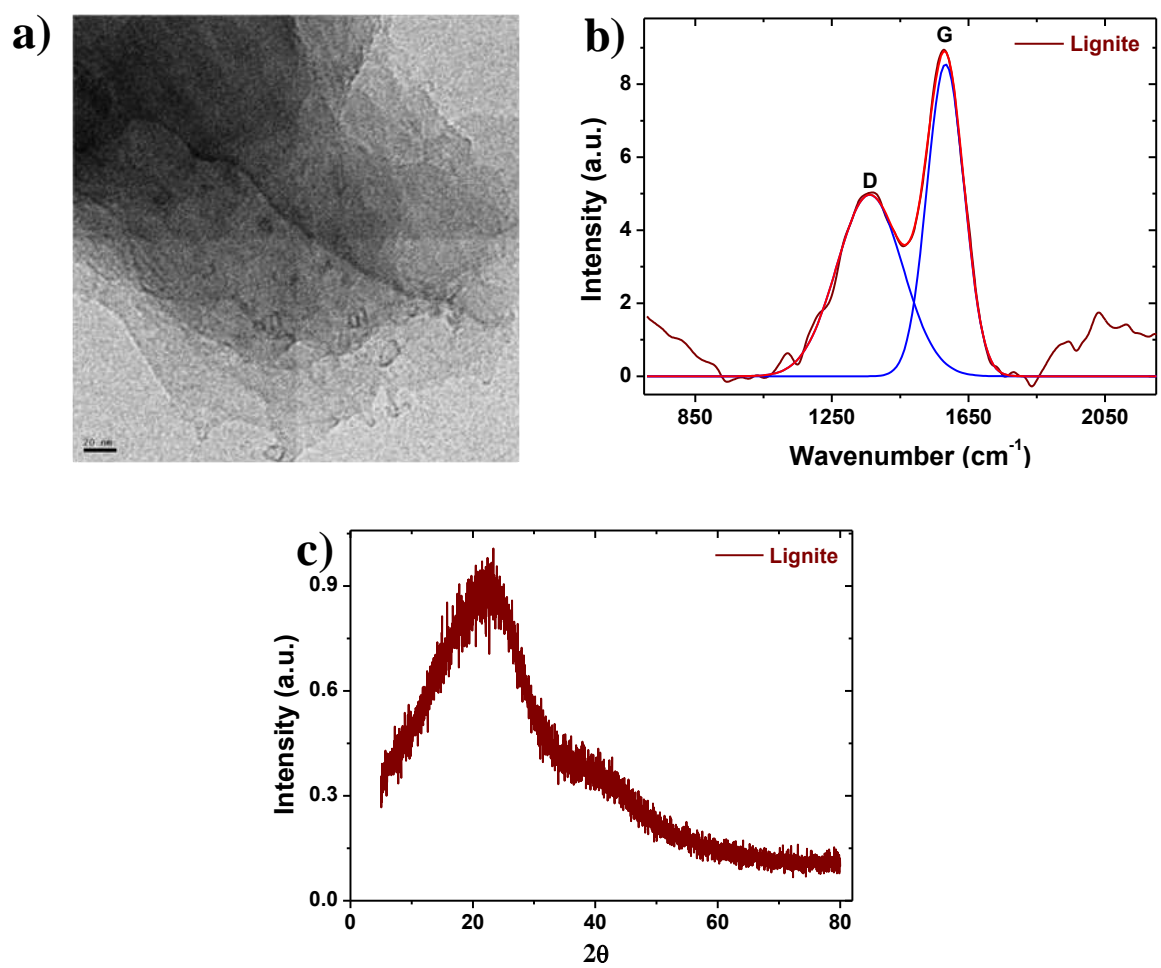


Figure S1. Characterisation of Lignite: **a)** TEM image of powdered lignite dispersed in ethanol and coated on a copper grid **b)** Raman spectrum of Lignite showing the characteristic D & G peak **c)** X-ray diffractogram of powdered Lignite

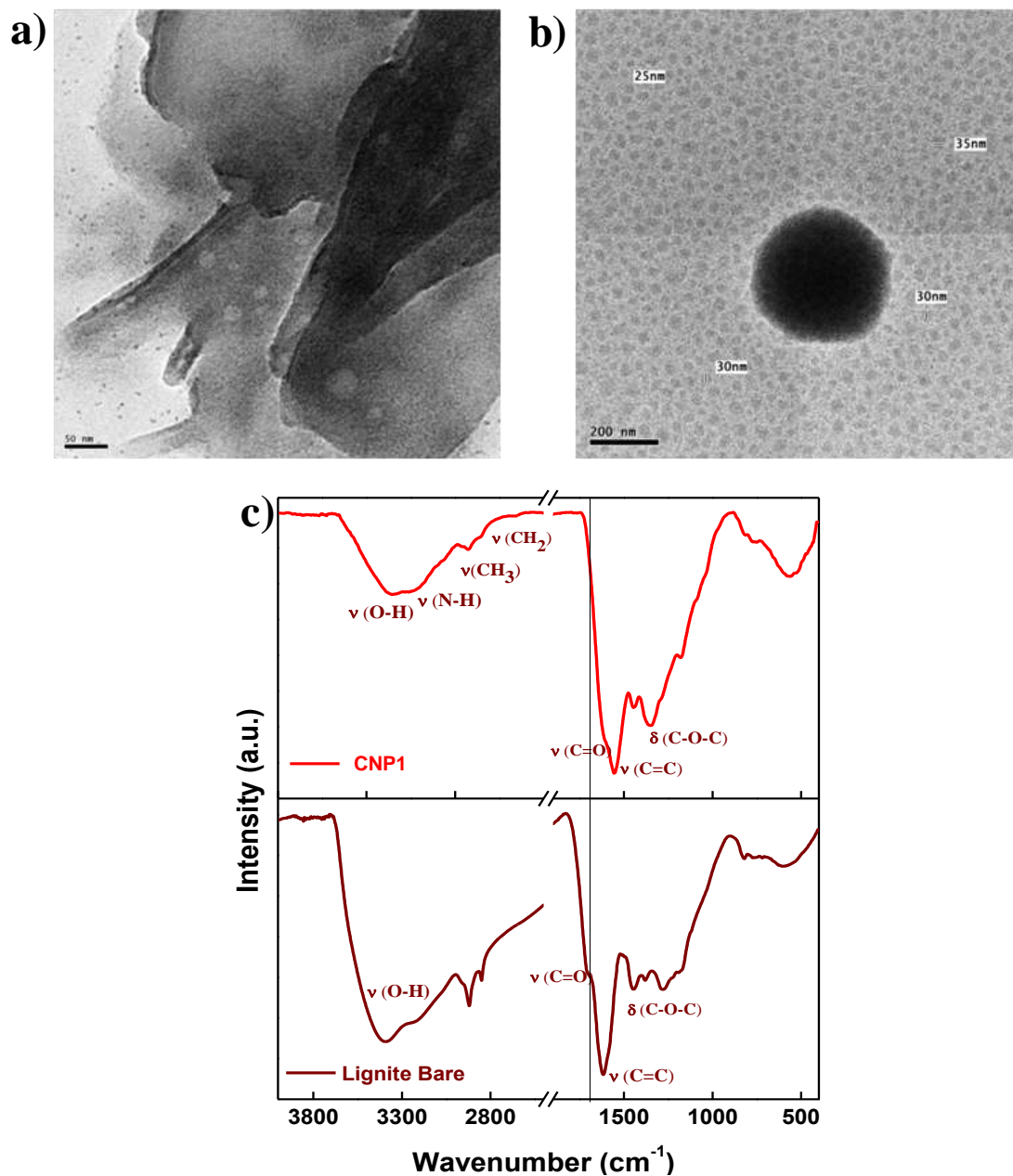


Figure S2. TEM image of **a)** Pristine solution obtained after reflux indicating the existence of both CNPs and layered structure of lignite **b)** Solution of CNP2 before ethanol extraction shows the existence of larger sized particles solubilised in 5 % EDA solution **c)** FTIR spectrum of Lignite and CNP1

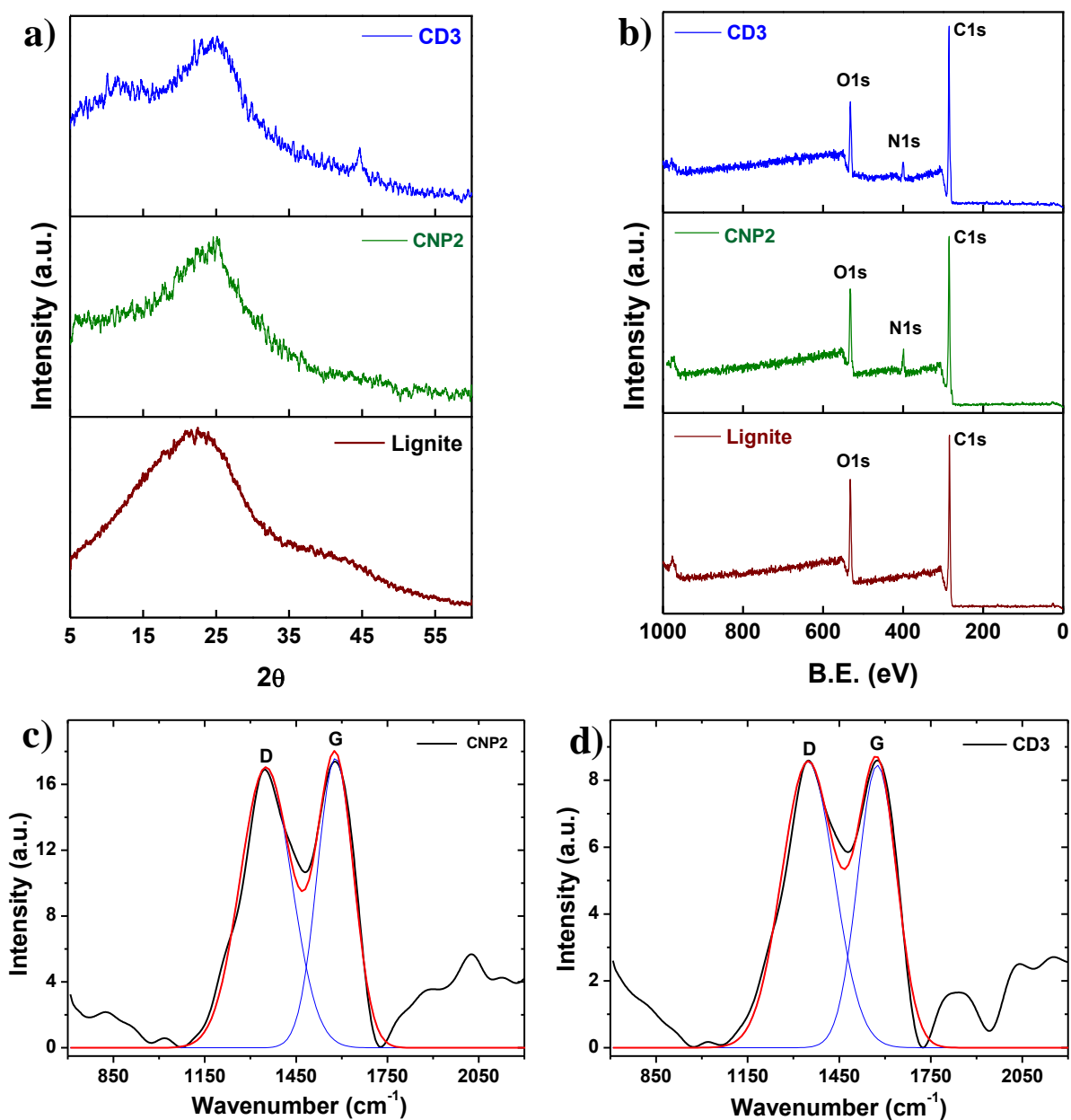


Figure S3. Characterisation of CNDs: **a)** X-ray diffractogram of powdered Lignite, CNP2, CD3 **b)** XPS survey spectrum of lignite, CNP2, CD3 **c)** Raman spectrum of CNP2 showing the characteristic D & G peak **d)** Raman spectrum of CD3 showing the characteristic D & G peak.

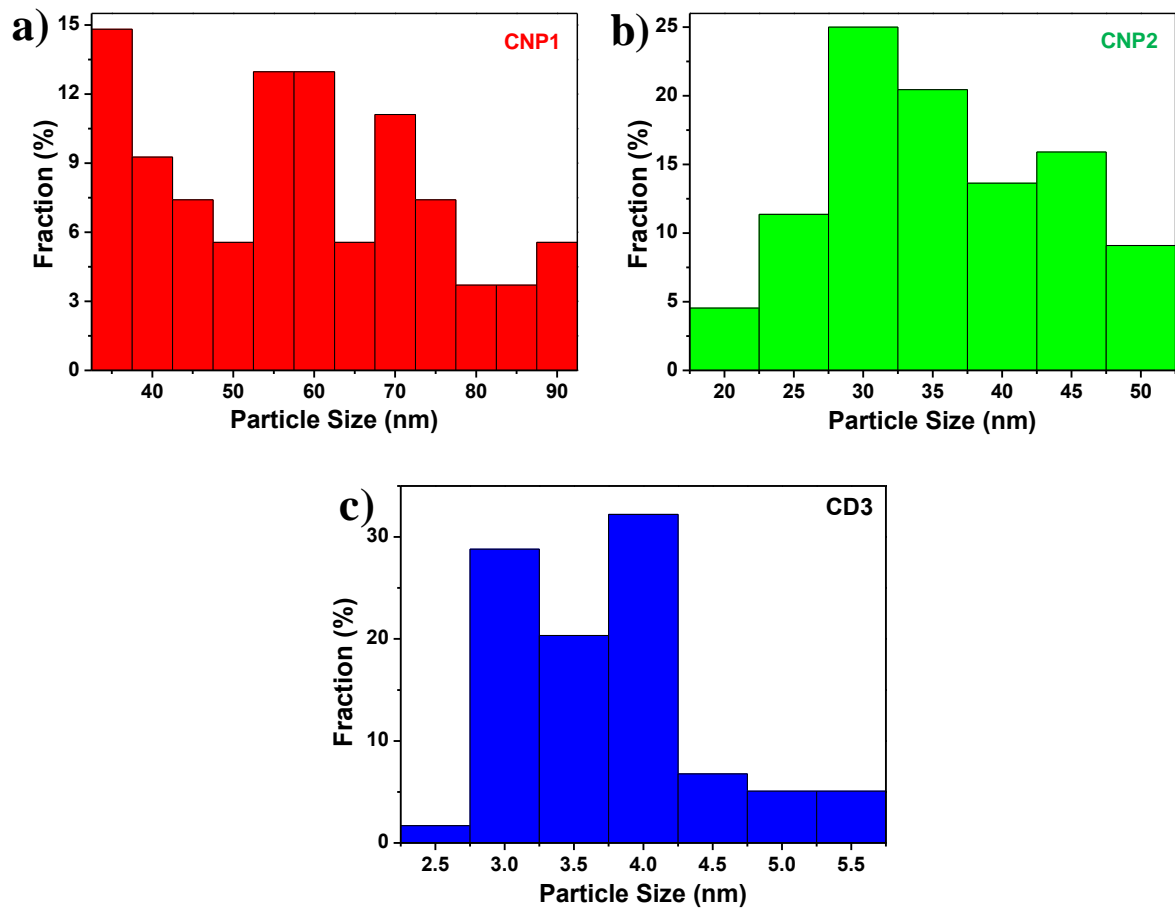


Figure S4. Statistical particle size distribution of **a) CNP1** **b) CNP2** **c) CD3**.

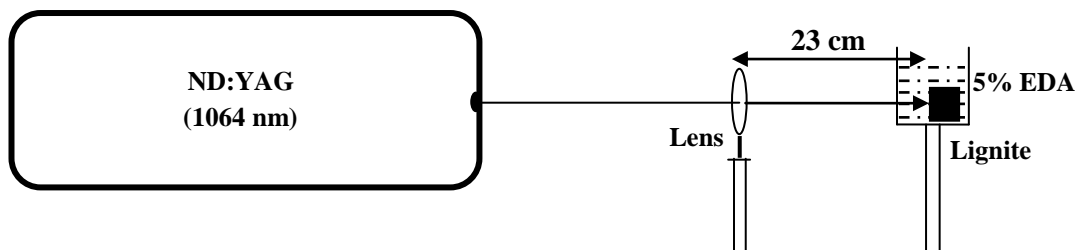


Figure S5. Schematic representation of experimental setup for PLA in 5% EDA solution.

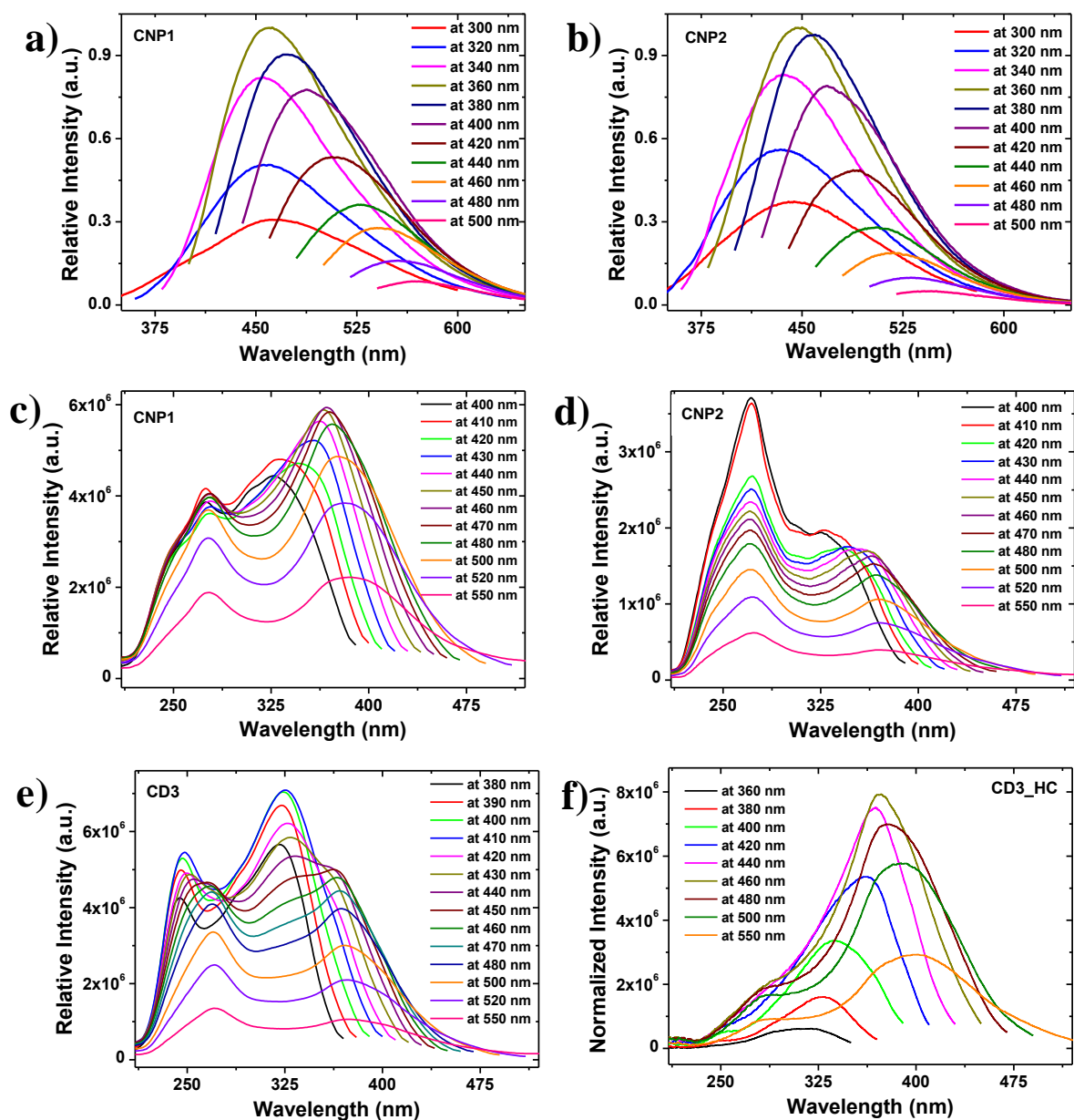


Figure S6. Excited Wavelength dependent emission spectrum of **a) CNP1** **b) CNP2**; Emission wavelength dependent excitation spectrum **c) CNP1** **d) CNP2** **e) CD3** **f) CD3_HC**

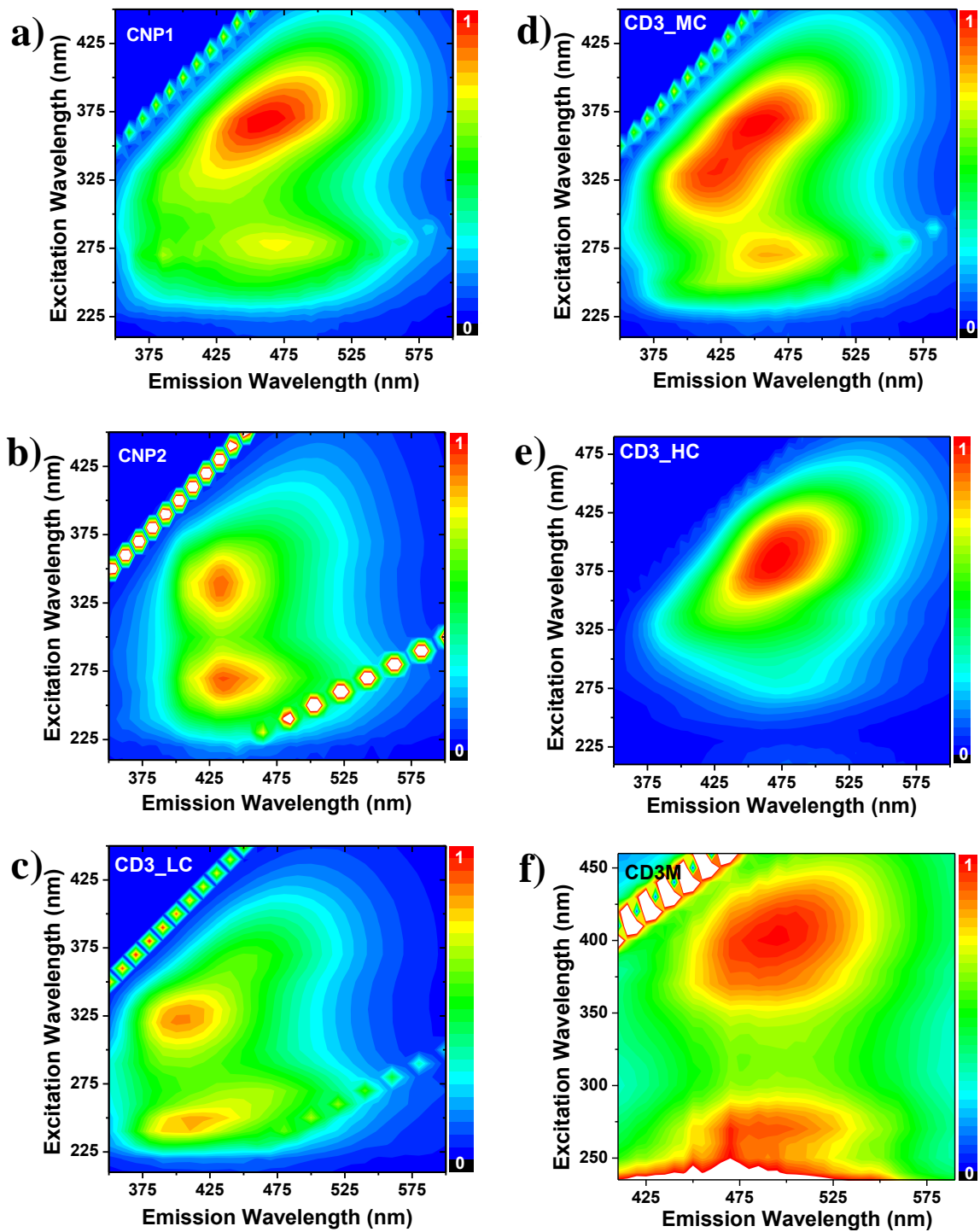


Figure S7. 2D Fluorescence Topographical Map of **a) CNP1** **b) CNP2** **c) CD3_LC (0.1 mg/mL)** **d) CD3_MC (0.4 mg/mL)** **e) CD3_HC (1mg/mL)** **f) CD3M**

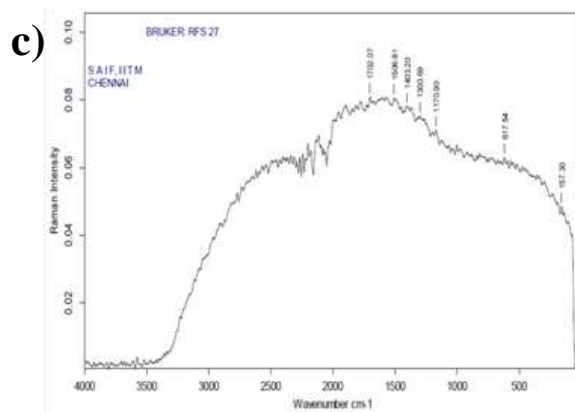
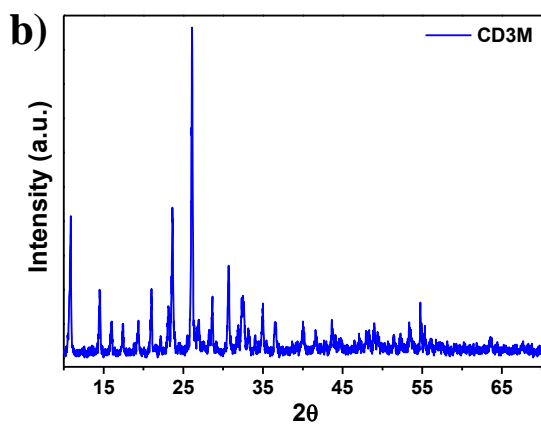
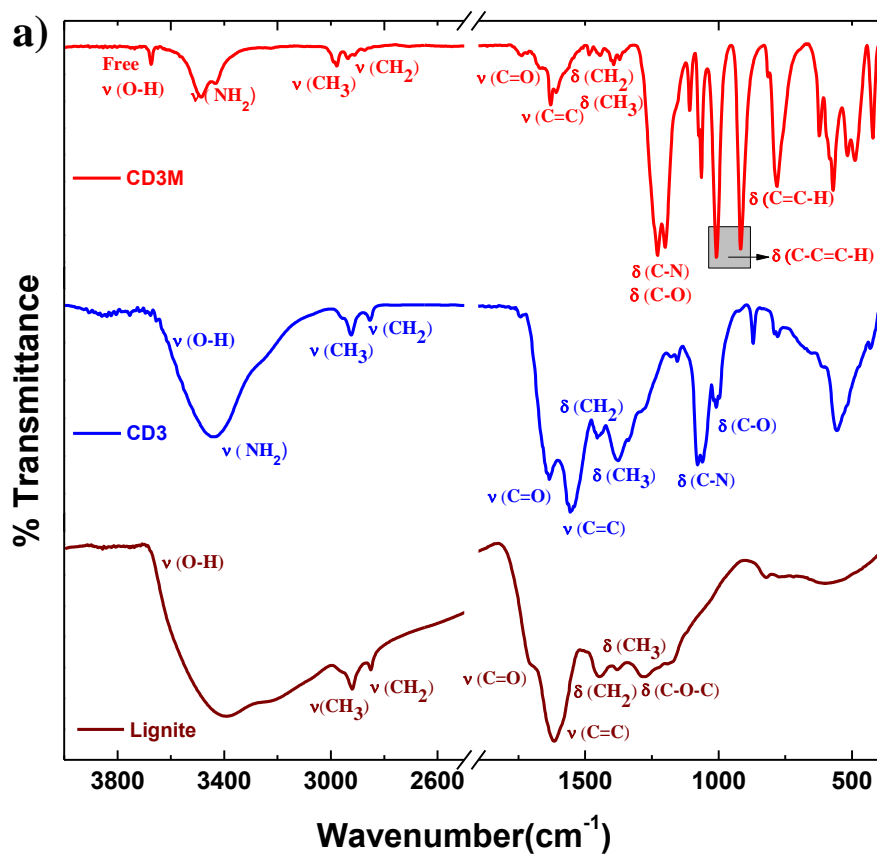


Figure S8. Characterisation of CD3M **a)** Stacked IR spectrum of Lignite, CD3, CD3M (from bottom to top) **b)** X-ray diffractogram of powdered CD3M **c)** Raman Spectrum of CD3M in solid state displaying broad band, characteristics of photoluminescent material.

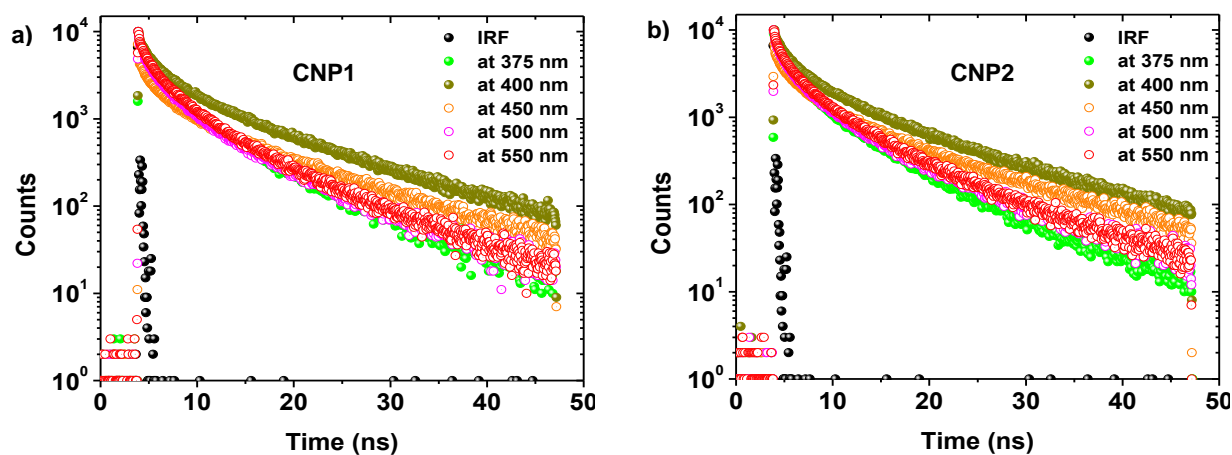


Figure S9. Fluorescence lifetime decay of a) CNP1 b) CNP2, recorded by exciting at 266 nm and monitored at different wavelength.

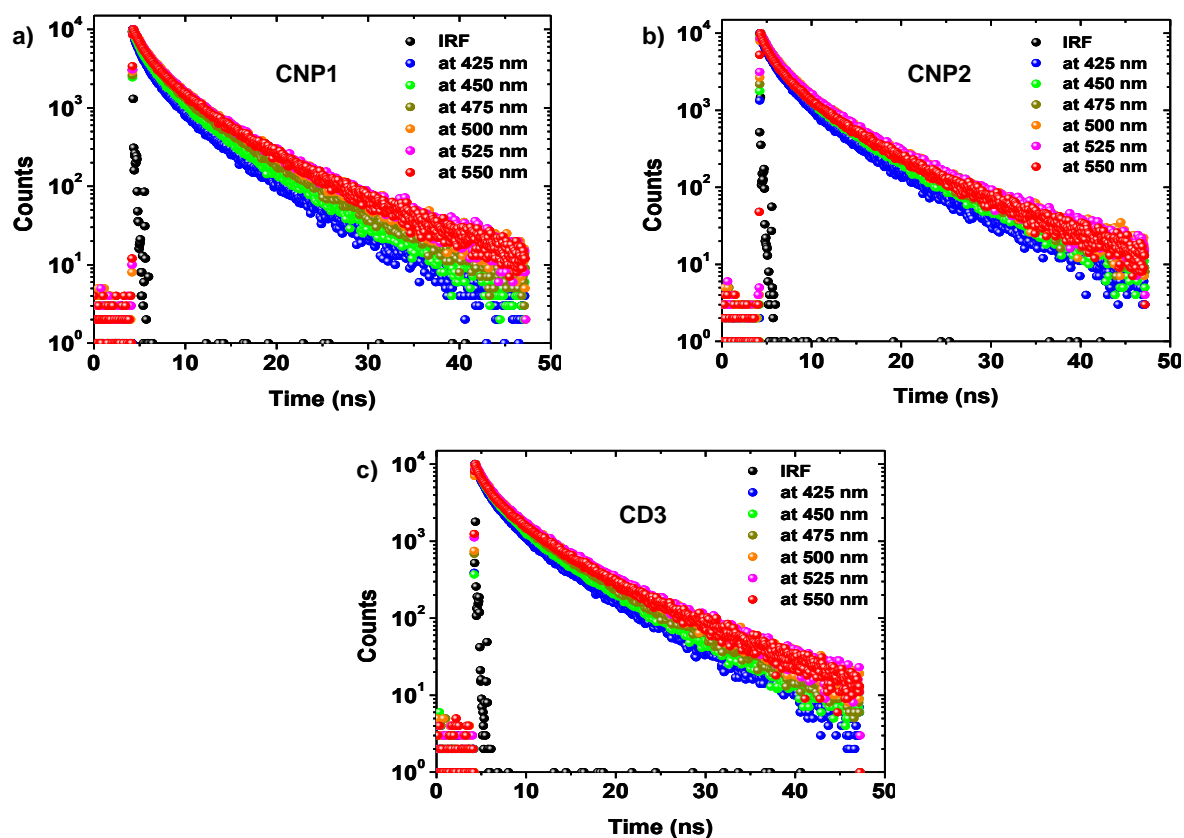


Figure S10. Fluorescence lifetime decay of a) CNP1 b) CNP2 c) CD3, recorded by exciting at 375 nm and monitored at different wavelength.

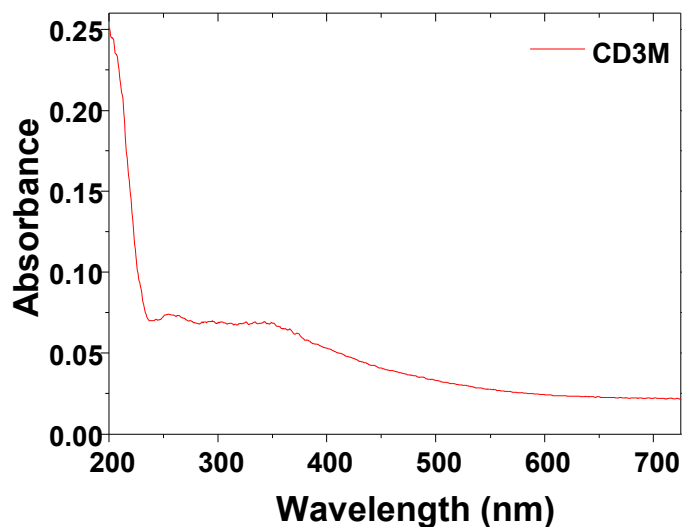


Figure S11. Absorption spectrum of CD3M measured through reflectance mode

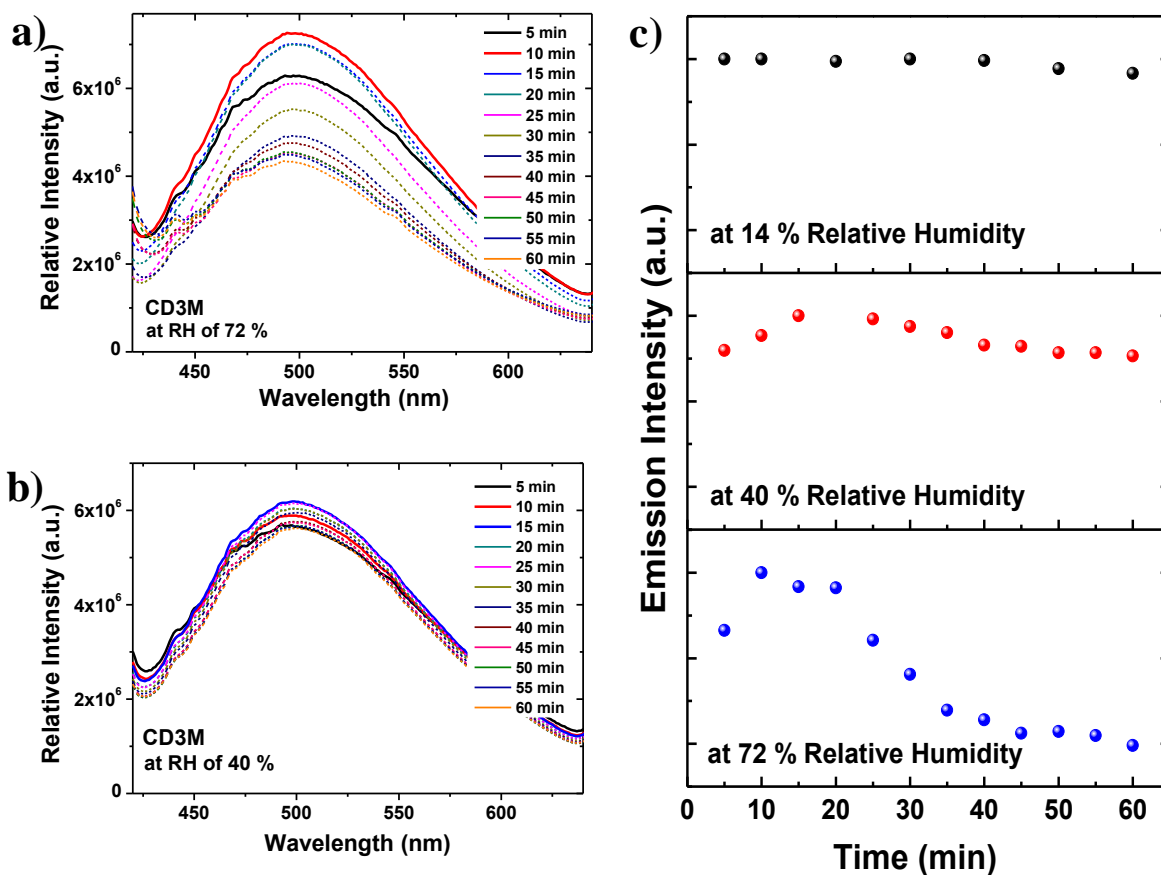


Figure S12. Variation in the emission spectrum of CD3M with respect to time at the relative humidity of a) 72 % b) 40 % c) Variation in the emission intensity of CD3M with respect to time at the relative humidity of 72 %, 40 % & 14 % (from bottom to top).

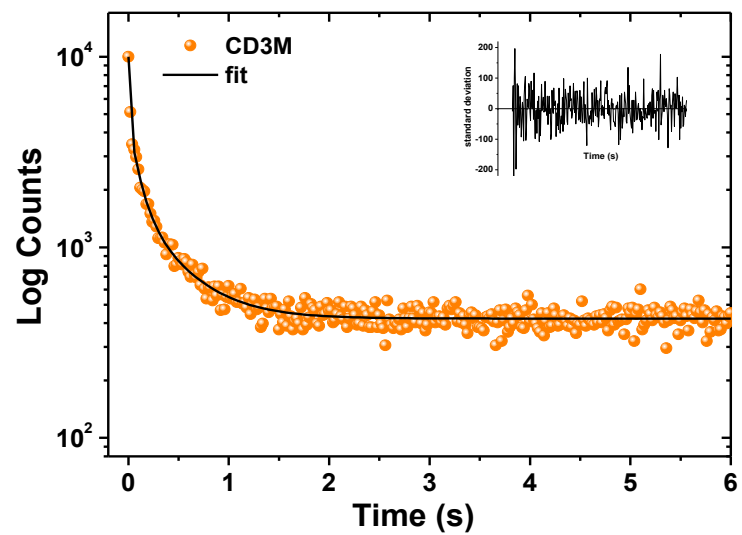


Figure S13. Phosphorescence lifetime decay of CD3M, recorded by exciting at 360 nm and the inset showing the corresponding standard deviation.

Table S1. Comparison of Infrared spectral data of Lignite, CNP2, CD3 and CD3M

Functional Group	Wavenumber (cm ⁻¹)			
	Lignite	CNP2	CD3	CD3M
Stretching:				
O-H	3680 - 3200 (<i>brd</i>)	3660 - 3200 (<i>brd</i>)	3650 - 3200 (<i>brd</i>)	3674 (<i>shp</i>)
N-H	-	3660 - 3200 (<i>brd</i>)	3650 - 3200 (<i>brd</i>)	3600 - 3300 (<i>brd</i>)
C-H (-CH ₃ & -CH ₂)	2920 & 2850	2926 & 2860	2922 & 2850	2978 & 2937
C=O	1707 (<i>str</i>)	1612 (<i>str</i>)	1633(<i>str</i>)	1670 (<i>w</i>)
C=C	1616 (<i>str</i>)	1573 (<i>str</i>)	1550 (<i>str</i>)	1630 (<i>w</i>)
C-O-C	1300 - 1050 (<i>brd</i>)	1300 - 1050 (<i>brd</i>)	1068 & 869 (<i>str</i>)	1210 (<i>str</i>)
Bending :				
-CH ₂ & -CH ₃	1445 & 1381	1448 & 1386	1454 & 1373	1465 & 1380
C-O	Merged inside the broad C-O-C band	Merged inside the broad C-O-C band	997	1006
C-N	-	Merged inside the broad C-O-C band	1009	1157

Table S2. Elemental composition of Lignite, CNP2 and CD3 obtained from XPS spectroscopy.

Element	Lignite (in %)	CNP2 (in %)	CD3 (in %)
Carbon	61.74	58.66	62.85
Oxygen	38.26	34.12	30.11
Nitrogen	-	7.22	7.04

Table S3. Steady state photophysical data of CNP1, CNP2, CD3 in water and CD3M in solid state.

Sample	λ_{abs}^{max} (nm)	λ_{emi}^{max} (nm)	ϕ_f (%)
CNP1	260, 325	468	4.5
CNP2	262, 323	435	5.1
CD3	222, 330	403	6.0
CD3M	254, 348	493	34.5

Table S4. Fluorescence Lifetime data of CD3 measured at different monitoring wavelength by exciting at 266 nm.

CD3								
Wavelength Monitored λ (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A1 (%)	A2 (%)	A3 (%)	τ_{avg} (ns)	χ^2
350	0.702	1.69	7.15	32.22	51.69	16.09	1.27	1.31
375	0.569	1.81	7.83	28.05	47.25	24.70	1.27	1.11
400	0.508	2.10	7.41	20.04	42.29	37.67	1.54	1.20
450	0.371	2.33	7.53	7.55	40.28	52.17	2.24	1.03
500	0.254	2.13	7.58	5.06	32.25	62.69	2.31	1.12
550	0.287	2.14	7.68	5.78	29.58	64.64	2.36	1.07

Table S5. Fluorescence Lifetime data of CNP2 measured at different monitoring wavelength by exciting at 266 nm.

CNP2								
Wavelength Monitored λ (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A1 (%)	A2 (%)	A3 (%)	τ_{avg} (ns)	χ^2
375	0.303	2.01	7.16	5.25	33.68	61.07	2.34	1.12
400	0.256	2.06	9.53	2.96	22.24	74.80	3.31	1.17
450	0.218	2.15	10.12	3.14	22.79	74.08	3.11	1.01
500	0.223	2.04	7.62	5.20	34.17	60.63	2.08	1.12
550	0.243	2.10	7.68	5.11	32.02	62.88	2.25	1.16

Table S6. Fluorescence Lifetime data of CNP1 measured at different monitoring wavelength by exciting at 266 nm.

CNP1								
Wavelength Monitored λ (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A1 (%)	A2 (%)	A3 (%)	τ_{avg} (ns)	χ^2
375	0.277	1.87	7.02	4.48	30.37	65.15	2.39	1.21
400	0.229	2.16	10.16	3.03	23.09	73.88	3.21	1.03
450	0.269	2.27	10.37	3.85	23.07	73.08	3.17	1.08
500	0.219	2.03	7.69	5.35	34.91	59.75	2.02	1.22
550	0.249	2.16	7.67	5.29	34.53	60.19	2.22	1.12

Table S7. Fluorescence Lifetime data of CD3 measured at different monitoring wavelength by exciting at 375 nm.

CD3								
Wavelength Monitored λ (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A1 (%)	A2 (%)	A3 (%)	τ_{avg} (ns)	χ^2
425	0.373	2.04	6.48	6.82	44.27	48.92	2.10	1.14
450	0.415	2.15	6.43	6.08	40.29	53.64	2.40	1.10
475	0.390	2.13	6.55	4.77	38.02	57.21	2.58	1.13
500	0.381	2.14	6.71	4.35	34.53	61.12	2.73	0.99
525	0.430	2.20	6.88	5.42	33.28	61.29	2.73	1.04
550	0.404	2.17	6.95	5.69	33.93	60.37	2.61	1.17

Table S8. Fluorescence Lifetime data of CNP2 measured at different monitoring wavelength by exciting at 375 nm.

CNP2								
Wavelength Monitored λ (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A1 (%)	A2 (%)	A3 (%)	τ_{avg} (ns)	χ^2
425	0.402	2.12	6.63	7.06	48.11	44.83	2.13	1.23
450	0.400	2.15	6.65	5.83	43.85	50.32	2.35	1.09
475	0.443	2.25	6.71	5.49	41.15	53.36	2.54	1.09
500	0.444	2.34	7.01	5.27	41.60	53.13	2.68	1.07
525	0.488	2.27	6.87	6.69	38.32	55.29	2.63	1.09
550	0.396	2.02	6.62	6.53	35.70	57.77	2.34	1.07

Table S9. Fluorescence Lifetime data of CNP1 measured at different monitoring wavelength by exciting at 375 nm.

CNP1								
Wavelength Monitored λ (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A1 (%)	A2 (%)	A3 (%)	τ_{avg} (ns)	χ^2
425	0.240	1.66	5.32	7.45	40.71	51.84	1.53	1.09
450	0.411	2.22	6.23	7.70	44.60	47.70	2.15	1.11
475	0.353	2.23	6.38	5.89	43.20	50.90	2.27	0.95
500	0.375	2.28	6.63	5.23	39.89	54.88	2.52	1.12
525	0.433	2.28	6.56	6.73	36.86	56.40	2.48	1.17
550	0.415	2.19	6.62	6.85	36.88	56.27	2.39	1.13

Table S10. Features of CNPs exfoliated from different carbon sources by Pulsed Laser Ablation.

Targeted Source	Product	Particle size	Quantum yield	Lifetime	Reference
Graphite powder blended with cement	Aggregated nano particles	5 nm	-	-	<i>J. Am. Chem. Soc.</i> , 2006, 128 , 7756
Graphite powder in PEG _{200N}	C-Dots	3.2 nm	5 %	NA	<i>J. Mater. Chem.</i> , 2009, 19 , 484–488
Carbon nano particles (~ 50 nm) in organic solvents	CQDs	< 10 nm	NA	NA	<i>Chem. Commun.</i> , 2011, 47 , 932–934
Carbon targets in water	CNPs	> 50 nm	NA	2.06 ns	<i>Sensors and Actuators B</i> , 2010, 145 , 702–707
¹³ C powder mixed with graphite cement	C-Dots	4-5 nm	20 %	NA	<i>J. Phys. Chem. C</i> , 2009, 113 , 18110.
Graphite powder in N-methyl pyrrolidone	C-Dots	1.5 - 3.5 nm	NA	NA	<i>Optical materials express</i> , 2012, 2 , 490.
Mixture of Benzene and Ni(II)oxide powder	GQDs	3.42	5.5 %	NA	<i>Carbon</i> , 2013, 64 , 341
CD3	CQDs	3.5 nm	6 %	~ 2 ns	In this work

Procedure for 2D fluorescence topographical mapping

2D fluorescence topographical mapping were recorded using Fluoromax 4P spectrofluorometer, by simultaneously scanning the excitation and emission monochromator in the excitation wavelength range 200 – 450 nm, with constant wavelength differences $\Delta\lambda$ (=10 nm) between them and emission spectra were recorded in the wavelength range of 350 - 650 nm in steps of 10 nm. Synchronous scan fluorescence mapping were plotted using Windows-based software Origin 7.5.